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Experimental and theoretical evidence and arguments are presented to justify a search for new superconductors, similar to the perovskite-based high temperature superconductors, but with the oxygen replaced by a chalcogen, that is sulfur, selenium or tellurium. Candidate compositions are proposed, together with methods of achieving their chemical synthesis. Safety and environmental issues were also analyzed. The work was performed as part of a Phase 1 SBIR project, sponsored by SDIO (BMDO) and managed by AFOSR.

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Final Report
Contract F49620-93-C-0025
Chalcogenide Superconductors -- A Search

1. Objectives

The objectives of the present Phase I SBIR investigation were to:

- 1) Justify a search for new superconductors that would be similar to the perovskite-based high temperature superconductors (HTS), but in which the oxygen is replaced by a chalcogen, that is sulfur, selenium or tellurium,
- 2) Propose possible compositions for such potential superconductors,
- 3) Search the literature for similar or related compositions,
- 4) Suggest alternative routes for achieving the chemical synthesis of specific compositions, and
- 5) Analyze safety issues and related costs for the proposed effort.

2. Rationale

The discovery of the perovskite-based, high temperature superconducting oxides promises to revolutionize electro-technology, particularly if materials with higher transition temperatures, higher critical magnetic fields, or greater usable (bulk) critical current densities can be found. We do not believe that the copper oxide (cuprate) compounds, which are at the center of most present-day investigations, are a singular "accident" of nature. To the contrary, there could well be many other quaternary, or higher order "multinary" chemical compositions that would also exhibit superconductivity. Moreover, if this should be true, it is indeed conceivable that we might discover critical fields and critical temperatures as high as, or even higher than the cuprate superconductors.

From a chemist's point of view, the obvious place to look for new superconductors would be to stay in the same column of the periodic table (#16, or VIA) and simply go from the oxides to the chalcogenides, *i.e.*, sulfides, selenides, or tellurides. It is well known that many simple binary transition metal chalcogenides are semi-conducting, while others exhibit metallic behavior, including superconductivity. Furthermore, the ternary Chevrel phase superconductors, exemplified by $PbMoS_6$, possess many desirable properties, in particular, very high critical magnetic fields, albeit at transition temperatures much lower than some of the HTS cuprates. However, the fact that there are few reports on other complex chalcogenide superconductors, or on chalcogenides with perovskite lattices, suggests that they may be difficult to prepare, unstable in the presence of air, moisture or carbon dioxide, or that they might disproportionate at atmospheric

pressure. Recurring controversial reports on T_c enhancements by anion substitutions in the cuprates could indicate similar effects, related to an inherent instability or reactivity of these superconducting chemical species.

It is also clear that chalcogenides introduce chemical hazards that are beyond the scope of the average physics laboratory facility. Indeed, in working with these materials, the deliberate and careful management of the potential chemical hazards associated with the chalcogens will have to be superimposed on the environmental, safety and disposal regulations that apply to the handling of "ordinary" heavy metal HTS compounds.

2.1. Materials Science

Our primary effort has been to search for, analyze and select various compositions with the appropriate defect or mixed valence characteristics that could lead to superconductivity. From the lessons learned on the HTS perovskites, we can predict that the most interesting and promising materials will **not** be stoichiometric, but rather exhibit fractional valence or what Matthias described as variable electron to atom ratios. The perovskite lattice tolerates and, perhaps, encourages partial substitution of elements at most cation lattice sites. When the elements are from the same column in the periodic table, the effect is one of changing the internal pressure, with a gradual change in T_c . On the other hand, when the elements are from different columns, there will be fractional changes in valence and the resulting changes in T_c are likely to be much more dramatic.

Our analysis of prospective structures has been based on the simple chemical perspectives of bond lengths, hybrid orbitals and electro-negativity. It is guided by the following arguments and procedures:

- 1) The crucial structural feature of presently known HTS materials are corner shared octahedra with copper in the center and oxygen at the apices. These octahedra are the main signature of (cubic) perovskites and related structures.
- 2) The resulting metal-oxygen chains can provide the superconducting path if the inter-atomic distances are short enough for an overlap of the appropriate electron wave functions **and** if the materials composition is such as to furnish itinerant metallic (collective or de-localized) electrons. The latter may be achieved by doping, by vacancies, or by a lack of stoichiometry.
- 3) We are not using the simple view that the anions (oxygen, sulfur, *etc.*) always exhibit a fixed valence of -2 and that any "oddness" must be associated with the variable valence of a transition element such as *Cu*. Indeed, modern band calculations do not restrict effective anion valences to integer values either.
- 4) The Periodic Table of the Elements, together with a table of crystal radii (sometimes called ionic radii) is our best guide for "cloning" materials with the desired properties.

- 5) The families of HTS oxides that are presently known are quite complex. The "game" of stacking cannon balls can only be a beginning, but it may be more enlightening to look at some of the structures as stacking sequences rather than as unique phases.
- 6) The substitution of chalcogenides for oxygen should be possible, but the generally larger radii of the latter may change the structures from cubic to hexagonal, or cause other distortions.
- 7) Chemists have searched for stable chalcoperoovskites since the 1950's. Our original search turned up only one reference: $BaZrS_3$, and perhaps $SrZrS_3$, and $CaZrS_3$ [A. Clearfield, *Acta Cryst.* **16**, 135-142 (1963)] The Ba compound is described as having metallic properties.
- 8) Analogous to the high temperature superconductor $BKBO$, $(Ba,K)BiO_3$, we propose to partially replace ("dope") some of the barium with potassium in the above compound. The Ba and K cations have nearly identical large radii of 1.5 Å.
- 9) The next step would then be to replace the tetravalent zirconium (0.86 Å) with a trivalent cation of similar size and similar electro-negativity.

Ion	At_Nbr	El_Neg	Radius
K^{+1}	19	0.8	1.52
Ba^{+2}	56	0.9	1.49
Ti^{+4}	22	1.5	0.745
Zr^{+4}	40	1.4	0.86
Al^{+3}	13	1.5	0.68
Sc^{+3}	21	1.3	0.885
Ga^{+3}	31	1.6	0.760
Y^{+3}	39	1.2	1.040
In^{+3}	49	1.7	0.940
La^{+3}	57	1.1	1.172
Tl^{+3}	81	1.8	0.81
V^{+3}	23	1.6	0.78
Cr^{+3}	24	1.6	0.76
Mn^{+3}	25	1.5	0.78
Cu^{+3}	29	1.9	0.68
Nb^{+3}	41	1.6	0.86
Ta^{+3}	73	1.5	0.86
O^{-2}	8	3.5	1.26
S^{-2}	16	2.5	1.70
Se^{-2}	34	2.4	1.84
Te^{-2}	52	2.1	2.07

- 10) The above Table lists various cations, their atomic number, Pauling electro-negativity values, and Shannon's crystal radii for the appropriate octahedral coordination of six.
- 11) The best match for zirconium turns out to be scandium, *Sc*, an element which up to now has not found any commercial applications. (Although its oxide is a by-product from uranium extraction, the annual consumption is only about 20 kg and the present price of scandium is about five times that of gold. The Air Force has, however, been interested in the metal as a structural material for space craft because of its high melting point and light weight).
- 12) The next best match would be *Ta*, provided that this transition element can be constrained (or "persuaded") to exhibit the valence of +3 (it normally prefers +4 or +5).
- 13) If size is the more important parameter, then subsequent choices would be *Nb*, followed by *Tl*, *V*, *Ga*, *Mn*, and *Cr*. The last choices would be *Al*, and *Cu*.
- 14) On the other hand, if electro-negativity is more important, the order would be *Mn*, *Al* first, *Ga*, *V*, *Cr*, *Nb* next and *Tl*, *Cu* last.
- 15) Some of these choices would not be valid if the presence of a transition element having multiple valence states is an essential feature of the HTS compounds, cf. item (3) in this list.

2.2 Literature Searches

We have recently done more extensive searches of the literature on ternary and higher order chalcogenides, using the on-line Chemical Abstracts data base (STN), as well as the CD ROM data bases JCPDS and LATTICE. This has shown that there is a great deal of activity worldwide on chalcogenides with possible uses in solar cells, infrared optical windows, batteries, photoluminescence, thermoelectrics, and blue-green lasers. But there is also significant competition in searching for new superconductors in this region of the periodic table. Much of that effort comes from very experienced academic "virtuoso" chemists/crystallographers, who relish creating novel crystal structures and who disdain any substance that cannot be produced as a single crystal.

The *Ba* compound referred to under item (7) in the above list is present, with newer neutron diffraction information confirming the older powder data, but it is described as orthorhombic rather than as a perovskite. However, we have found nothing on any mixed *Ba-K* compounds, as suggested in item (8) of the list. Nevertheless, the idea of trying to dope known structures is suggested by a number of investigators.

We have also just become aware of a paper by K. A. Mueller, entitled "Recipe for high- T_c transition-metal chalcogenide superconductors" [*Materials Chemistry and Physics*, 33, 171-175 (Mar 1993)], where he enumerates seven conditions for high T_c , as demonstrated by the cuprates. Mueller's recipe is:

- (1) Distorted perovskite with layered CuO_2 sheets,
- (2) Transition metal ion with a strong Jahn-Teller effect,
- (3) Doping of the insulating CuO_2 layers from acceptors or donors in adjacent layers,
- (4) Hole doping on the oxygen p-orbitals for highest T_c , a consequence of the large Coulomb repulsion energy, or Hubbard energy (U) between the holes and the transition metal ion,
- (5) Near matching of the of the chalcogenide p- and transition metal d-levels, so that the charge transfer energy is less than U ,
- (6) A large polarizability of the anion, and
- (7) Antiferromagnetism of the undoped CuO_2 sheets.

Nothing in Mueller's analysis conflicts with our list of arguments in Section 2.1, except for his greater emphasis on transition metal anions, *cf.* our item (15). Nor does he really favor the higher chalcogenides (*S*, *Se*, and *Te*), except when discussing polarizability, where he states guardedly: "Perhaps S^{2-} might be a better candidate, but here again oxygen **so far** (our emphasis) seems the optimum chalcogenide anion." In short, we find these recipes by the High T_c Nobel Laureate quite encouraging for our proposal.

2.3 Inorganic Chemistry

The options for synthesizing the desired compounds, include direct synthesis from the elements and conversion from the oxides in a stream of hydrogen sulfide gas, H_2S , or carbon disulfide, CS_2 . On the other hand, it is probably simpler to start with mixtures of the binary chalcogenides, specifically sulfides, and then try to form the complex compounds at elevated temperatures by diffusion in the solid state, by vapor transport in the gas phase, or by crystallization from a flux of mixed salt or molten sulfur. Suitable containers would be silica (fused quartz) tubes for the vapor transport, ceramic or graphite crucibles for the mixed salt process and sealed metallic capsules for the molten sulfur process. For the capsules, a furnace that can provide pressure containment and multiple layers of protection, such as a Hot Isostatic Press (HIP), would be best. We believe that the temperature range of 600 to 1050C should be the starting point in attempting these syntheses.

It is very likely that the stability range of the desired perovskite phases will be quite narrow in terms of composition and temperature of formation. Furthermore, we have to be aware of and try to utilize either chalcogen deficiencies or excesses in our doping attempts. This means that for a systematic study at least four to six mixtures will have to

be prepared for each cation of interest and that each composition will have to be subjected to a number of different heat treatment and quenching protocols.

We also have to be prepared for the decomposition of any of the new compound, due the presence of air, moisture, or CO_2 into poisonous gases or vapors, such as H_2S , or SO_2 . We, therefore, have to be able to handle and transfer the materials in an inert environment and we may have to encapsulate them, possibly in gold foil, during their characterization.

2.4 Physical Measurements

Clearly, there will be a premium on **quickly** screening 10 to 50 milligram quantities of the new materials for their superconductivity, as soon as they have been prepared and possibly while still in their silica tubes. It is obvious that a speedier method than conventional SQUID magnetometry would be desirable. On the other hand, it could well turn out to be unwise to give up the sensitivity of the SQUID procedure, but neither is there any need or advantage in doing the screening in a 5T magnet operated at 1mT (10 Oe). This then suggests a sensitive AC susceptometer with a simple helium flow cryostat and a heater to produce fast temperature sweeps.

If we succeed in finding new superconductors, we will, of course, want to establish their crystal structure. Such studies will have to be done on a cooperative basis with an academic or government institution.

3. Proposal

In order to get ready for and carry out the proposed research and to prepare and evaluate 15 to 20 samples per month, we envisage the following tasks:

3.1 Task 1 -- Glove Box

Modify an existing glove box with a better airlock and a purified Argon gas supply. Install milligram balance and small pellet press.

3.2 Task 2 -- Quartz Blowing

Obtain and set up torch and other equipment for evacuating and sealing the sample containing silica (fused quartz) tubes.

3.3 Task 3 -- Furnaces

Equip two available small tube furnaces with programmable temperature controllers.

3.4 Task 4 -- Chemical Techniques

Check out the proposed methods of high temperature chemical synthesis and associated handling procedures by synthesizing the "parent" compound listed in item 7.

3.5 Task 5 -- AC Susceptometer

Assemble or acquire access to a high throughput AC susceptometer for the 4-300K range.

3.6 Task 6 -- Safety and Environmental Compliance

Set up monitoring equipment to guarantee and document compliance with all environmental and safety regulations. We have ascertained that the disposal costs for the materials of interest will equal or, possibly, exceed their acquisition costs, especially for the 50 to 100 gram quantities that are envisaged.

3.7 Plans

As of the time of this writing, we have not as yet decided under what format to continue the present effort. The options will depend on the judgment and programs of the funding agencies and could be either a Phase II SBIR using a CRADA, or an STTR with closer cooperation and coordination between our small business and a governmental organization. At any rate, we intend to continue exploring the most promising concepts under company funding.